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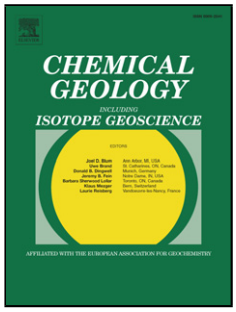

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PII: S0009-2541(19)30479-6

DOI: https://doi.org/10.1016/j.chemgeo.2019.119350

Reference: CHEMGE 119350

To appear in:

Received Date: 23 June 2019

Revised Date: 20 October 2019

Accepted Date: 25 October 2019

Please cite this article as: { doi: https://doi.org/

U-loss associated with laser-heating of hematite and goethite in vacuum during (U-Th)/He dating and prevention using high O_2 partial pressure

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Abstract

Single-aliquot (U-Th)/He dating of hematite has been used to study iron-oxide precipitation in various environments, but we show there is an important challenge to the method: highly retentive hematite samples require temperatures of >1000 °C to be completely degassed, whereas the temperature for major U-loss is ∼980 °C. This leads to erroneously high (U-Th)/He ages. Through the analysis of U, Th, and Sm of hematite and goethite samples, we show the degree of U-loss at this temperature and demonstrate that prolonged heating at temperatures of 950 °C can lead to U-loss. We show that loss of U in goethite and hematite samples is associated with phase change from hematite to magnetite as Fe is reduced. The onset temperature of vacuum reduction of hematite can be increased from about 800-900 °C in vacuum to approximately 1250 °C in an oxygen partial pressure of 100 mbar. We show that samples can be outgassed to extract helium at 1150 °C without U-loss in an O_2-rich atmosphere during heating, which does not increase the

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analytical blanks. We describe our implementation and automation of the procedure. An average age calculated on a reference hematite sample from replicate aliquots (n=12), which were analyzed using this procedure, has a relative uncertainty of 2% (1σ), and is within uncertainty of the previously measured two-aliquot age. We suggest this O_2 degassing procedure as a way to precisely and reproducibly determine single-aliquot hematite and goethite (U-Th)/He ages.

Keywords: hematite, goethite, (U-Th)/He dating, single-aliquot, geochronology

1. Introduction

(U-Th)/He geochronology and thermochronology of hematite has been used to quantify the time-scales of lateritic weathering (Pidgeon et al., 2004; Danišík et al., 2013; Cooper et al., 2016; Wells et al., 2019), fault activity (Adams et al., 2013; Evenson et al., 2014; Ault et al., 2015, 2016; McDermott et al., 2017; Moser et al., 2017; Calzolari et al., 2018; Garcia et al., 2018), episodes of hydrothermal mineralization (Wernicke and Lippolt, 1993, 1994a,b; Bähr et al., 1994; Lippolt et al., 1995; Wernicke and Lippolt, 1997; Farley and Flowers, 2012; Farley and McKeon, 2015; van den Kerkhof et al., 2018; Jensen et al., 2018; Wu et al., 2019), and diagenetic cementation (Reiners et al., 2014). Highly retentive hematite samples must be heated to >1000 °C to completely degas helium (e.g. Farley and Flowers, 2012; Farley and McKeon, 2015). In goethite, which transforms to hematite around 180-300 °C (Prasad et al., 2006; Ruan et al., 2001) and is therefore present as hematite at goethite degassing temperatures (800-1000 °C), a substantial loss of U

has been documented (Vasconcelos et al., 2013). Therefore, we also expect U-loss in hematite due to sample heating, which leads to erroneously high (U-Th)/He ages. The origin of this U-loss is not currently known, but it may involve U-volatilization and removal from the sample. In some cases, volatilization of bulk material (Fe, Mn, Cu, Pb, etc.) has been observed as well (Garcia et al., 2018).

In order to circumvent the problem of U-loss, some studies have employed the two-aliquot approach (Strutt, 1909; Bähr et al., 1994; Wernicke and Lippolt, 1993, 1994b,a; Pidgeon et al., 2004), by which analyses of parent and daughter isotopes are performed on separate aliquots. In the two-aliquot approach, a large amount of material (tens of milligram to gram quantities) is crushed and homogenized. An aliquot of this material is weighed and heated to 1200-1400 °C (Wernicke and Lippolt, 1994b; Bähr et al., 1994; Farley and Flowers, 2012; Farley and McKeon, 2015) to achieve complete degassing of helium, which is measured using a noble gas mass spectrometer. A different aliquot is analyzed for parent isotope concentrations (e.g. Farley and Flowers, 2012; Farley and McKeon, 2015; Wu et al., 2019), usually by isotope dilution inductively-coupled plasma mass spectrometry (ICP-MS) after acid dissolution. Separately measured He, U, Th, and Sm concentrations are then used to compute a single (U-Th-Sm)/He age.

However, a large amount of sample is required to perform separate measurements because of the need for homogeneous material. Homogenization of sample material obliterates any inhomogeneity in parent or daughter isotopes, which might be of interest. Any actual age heterogeneity in the sample is reduced to an average age, which might not be geologically meaningful.

Single-aliquot (U-Th)/He dating, in which ^{4}He and parent isotopes are measured on the same aliquot, is the preferred approach for geochronology and thermochronology of apatite (Wolf et al., 1996), zircon (Reiners et al., 2002), and other phases. Aliquots of typically 10-100 µg are laser-heated in Pt or Nb packets to release He. After the helium measurement, the sample inside the packet is dissolved. Parent isotopes are measured by isotope dilution, along with determination of the mass of the sample based on mineral stoichiometry. Since both parent and daughter isotopes are measured on the same aliquot, a (U-Th)/He age is calculated from absolute amounts of U, Th, Sm, and ^{4}He in the sample.

Single-aliquot dating has several advantages over the two-aliquot method. Since there is no need for homogenization, the required sample masses are much lower. Inhomogeneity in parent and daughter isotopes is taken into account, since helium and U/Th/Sm are measured on the same material. This permits age determination with high spatial resolution, which is especially useful for layered iron-oxide deposits, such as pisoliths, which display significant age heterogeneity on length-scales of tens of micrometers (e.g. Hofmann et al., 2017). These samples might not yield enough sample material for the application of the two-aliquot method, leaving the single-aliquot method as the only feasible way to determine meaningful (U-Th)/He ages.

If any U or Th, or even sample material, was lost before the dissolution step, the absolute amounts of parent isotopes would be deficient relative to the amount of extracted ^{4}He and ages would appear anomalously high. Extraction temperatures for (U-Th)/He dating are chosen by individual laboratories based on the phase – about 940 °C for goethite (Shuster et al., 2005), 1050

°C for apatite (Wolf et al., 1996), 1200 °C for zircon (Reiners et al., 2002), and 1280 °C for titanite (Reiners and Farley, 1999) — so as to reliably and quantitatively extract He. Potential volatilization of parent isotopes due to heating has been a concern since the initial development of the (U-Th)/He method. For apatite, Wolf et al. (1996) showed no measurable loss of U or Th at 1100 °C. Zircon has been shown to retain U at temperatures of 1300 °C (Reiners et al., 2005). Major loss of U as a result of direct laser-heating has been documented in titanite (Reiners and Farley, 1999).

Extraction time and temperature required to completely degas helium from a mineral are dependent on its He-retentivity. In goethite, U is lost while Th is retained at high temperatures (Vasconcelos et al., 2013). This effect can be documented by heating aliquots of the same sample, which should yield the same ages, to different temperatures and expressing the outcome as an apparent age. Figure 1 shows a theoretical example. More helium is extracted with increasing temperature, leading to an increase in apparent age. As U-loss occurs at high temperatures, the resulting age of aliquots increases rapidly. In samples in which effective uranium concentration (eU) is dominated by U, the apparent age will tend to infinity for complete U-loss. With Th or Sm present, the age will increase to a value higher than the age of the sample. Ideally, U-loss will occur at temperatures well above the temperature for complete helium extraction, which will define a plateau accurately corresponding to the 'true' (U-Th)/He age of the sample (Vasconcelos et al., 2013). If U-loss occurs at temperatures below those required for complete helium extraction, there is no plateau (Fig. 1) and, consequently, no 'safe' temperature range for sample degassing.

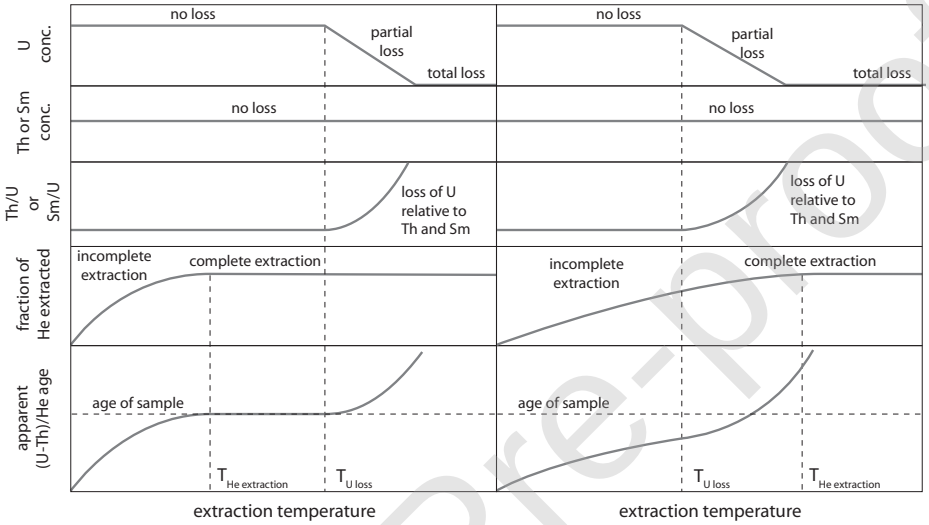

Figure 1: Theoretical heating experiment with U-loss in an ideal case (left) and a problematic case (right). Below the He extraction temperature, ages are lower than the 'true' age of the sample due to incomplete helium extraction. U is lost at high temperatures, which leads to an increase in age as well as Th/U and Sm/U ratios. Age will tend to infinity for complete U-loss, unless Th is present. In an ideal case, complete helium degassing occurs at temperatures lower than that of U-loss. Samples can be safely degassed in the temperature range of the plateau between the He-extraction and U-loss temperatures. If U-loss occurs at temperatures above that of complete He extraction, there is no plateau and the age of the sample cannot be accurately determined.

Vasconcelos et al. (2013) performed this experiment on one goethite sample, which fully degassed when heated to around 925 °C for 6 min. Apparent ages increased above the bulk age of the sample between 1050 °C and 1100 °C, along with a significant increase in the Th/U ratio. In the case of this goethite, the required He-degassing temperature seems to be significantly lower than the U-loss temperature. If the result is representative, then goethite samples can be degassed at an intermediate temperature, ensuring complete helium extraction without U-loss. The same pattern of U-loss in goethite and hematite samples heated to high temperatures has been observed in subsequent studies (e.g. Reiners et al., 2014; Garcia et al., 2018; van den Kerkhof et al., 2018).

In this study, we perform the same type of heating experiment on small aliquots (5-200 µg) of hematite to find optimal extraction parameters while preventing U-loss, thus enabling a single-aliquot methodology similar to that for goethite. We show that U-loss correlates with the phase transition from hematite to magnetite, which occurs in hematite and goethite samples heated in vacuum. Furthermore, we demonstrate that the temperature of phase transition can be increased and U-loss can be prevented by degassing samples in an atmosphere of pure O_2. We describe how this method can be implemented and automated for routine single-aliquot dating of hematite and goethite samples.

2. Experimental setup and samples

We performed experiments with two basic setups to degas samples (a) in vacuum while exposed to a charcoal trap cooled with liquid nitrogen (LN_2),

and (b) in a pure O_2 atmosphere of about 130 mbar. Laser heating, helium measurement, sample dissolution, and elemental analysis followed the standard procedures for goethite at Caltech described by Hofmann et al. (2017).

2.1. Samples

We performed heating experiments on hematite samples with well-established two-aliquot (U-Th)/He ages and (U-Th)/Ne ages (Tab. 1). They represent a wide range of ages (130-1760 Ma), as well as U and Th concentrations (0.2-15 ppm). These values were determined by previous studies on bulk samples of at least several milligrams (see Tab. 1). We adopted abbreviations for samples used in previous studies. HM1 (13-N64 'Black Rock') and HM2 (03QK-90 'Beeshoek') are massive iron ore samples from boreholes (Miller, 2019), MS (CIT-10443, MI-43) is botryoidal hematite from the Pabst Mine in the Gogebic Range, Michigan (Farley and McKeon, 2015), GC (CP06-1 P300) is a hydrothermal hematite sample from the Redwall Limestone of the Grand Canyon (Farley and Flowers, 2012), and HM2048 (CIT-2048) is sample material derived from crushing a single-crystal hematite from Minas Gerais, Brazil (Farley, 2018).

Additional samples were used to probe the effect of laser-heating and O_2 degassing on goethite (Tab. 1). The following goethite samples with ages of 10-64 Ma were analyzed in this study: blade (DMNH-10029) is from a sample with radiating blades of goethite on massive quartz (Miller, 2019), Lyp (LynP02-09-A2) and RH (Roy-02-02-C3) are from a banded vein and a massive block of goethite from a channel iron deposit (Vasconcelos et al., 2013), YAN (YAN-02-01-A) is vitreous goethite cement from a channel iron deposit (Heim et al., 2006), and sample CIT (CIT-16406) is a banded goethite sam-

ple from the Igarape Bahia Mine, Carajas, Brazil obtained from the Caltech Mineral Collection.

2.2. Helium-4 measurement

Samples were loaded into Pt tubes of 1 mm length and 0.6 mm in diameter and the ends were pinched shut to produce flat packets. These packets were heated with a diode laser in vacuum while exposed to a charcoal trap submerged in LN_2. Temperatures during heating were monitored using a one-wavelength pyrometer, which was calibrated by laser-heating a Pt packet enclosing a K-type thermocouple under both vacuum and O_2 conditions (for details see Supplementary Material B). This empirical calibration was used to determine temperatures by optical pyrometry to within 2-3% (5-20 °C). The stated uncertainty takes into account slight differences in emissivity between different packets and changes in emissivity as a result of repeated heating cycles (see Supplementary Material B).

We heated individual aliquots to a temperature between 600 °C and 1450 °C, in most cases for 10-20 min. The resulting ^{4}He was spiked with pure ^{3}He and cryogenically fixed. The ^{4}He/^{3}He ratio was measured using a Pfeiffer Vacuum Prisma QMS 200 quadrupole mass spectrometer. Absolute amounts of ^{4}He were determined relative to a standard with a known amount of ^{4}He. Standards and procedural blanks were interspersed every 3-6 sample measurements to track instrumental drift. We amended this setup for degassing of samples in a pure O_2 atmosphere. In early experiments, we heated CuO packets to liberate O_2, which produced oxygen partial pressures <1 mbar. To increase the phase transition temperature even further and to automate the extraction process, we connected an O_2 tank with a pipette to the exist-

Table 1: Hematite and goethite samples used in this study. Ages and concentrations of hematite samples are bulk values determined by the two-aliquot method on several milligrams of sample material, as reported in the original references. Values for goethite samples represent the average of several aliquots of tens to hundreds of micrograms.

Hematite Samples											
Sample	Sample Name	Reference	(U-Th)/He [Ma]	(U-Th)/Ne [Ma]	^{4}He [nmol/g]	U [ppm]	Th [ppm]	Sm [ppm]	eU [ppm]	Th/U	Sm/U
HM1	Black Rock	Miller (2019)	1523±61	1706±141	3.54±0.15	0.26±0.01	0.50±0.01	0.63±0.02	0.38±0.02	1.9231	2.4231
HM2	Beeshoek	Miller (2019)	1761±39	1776±97	14.42±0.02	1.03±0.02	1.08±0.01	0.26±0.01	1.28±0.02	1.0485	0.2524
MS	CIT-10443	Farley and McKeon (2015)	571±18	756±18	22.80±0.60	7.00±0.11	0.01±0.01	0.88	7.00±0.11	0.0014	0.1257
GC	CP06-1 P300	Farley and Flowers (2012)	130±1.7	217±5	14.10±0.20	15.70±0.20	14.90±0.10		19.20±0.22	0.9490	
HM2048	CIT-2048	Farley (2018)	not reported								
Goethite Samples											
Sample	Sample Name	Reference	(U-Th)/He [Ma]	(U-Th)/Ne [Ma]	^{4}He [nmol/g]	U [ppm]	Th [ppm]	Sm [ppm]	eU [ppm]	Th/U	Sm/U
blade	DMNH-10029	Miller (2019)	not measured								
Lyp	LynP02-09-A2	Vasconcelos et al. (2013)	30.7±1.6		9.7	36.8				2.49	
RH	Roy-02-02-C3	Vasconcelos et al. (2013)	63.9±6.4								
YAN	YAN02-01-A	Heim et al. (2006)	10±0.3							1.08	
CIT	CIT-16406	this study									

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ing vacuum degassing system to deliver oxygen partial pressures between 30 mbar and 150 mbar. We performed heating experiments of both hematite and goethite samples with this setup. Implementation of this method is discussed below and further details can be found in Supplementary Material A.

2.3. Sample dissolution and elemental analysis

After degassing, samples in Pt packets were transferred to a Teflon vial and 100 µl of concentrated HCl as well as 100 µl of a spike solution containing ^{235}U and ^{230}Th for isotope dilution and Ru for internal standardization was added. The Teflon vials were capped and refluxed on a hot plate at 150 °C for at least 12 hours. We did not observe any insoluble residue, showing that samples were completely dissolved by this procedure. Solutions were dried on a hot plate at 95 °C, and the resulting salts were dissolved in 50 µl of concentrated nitric acid, and diluted with 1 ml of MilliQ water. Elemental analysis of U, Th, Sm was performed by isotope dilution, and Fe, Mn, Al, and Si were measured with Ru as an internal standard using an Agilent 8800 ICP-MS.

We improved the precision and accuracy of the Fe-based sample mass measurement by using Ru instead of Ca as an elemental spike for ICP-MS. The precise and accurate determination of Fe-based sample mass is vital for detecting absolute U-loss, because U concentrations are calculated using Fe-based mass. We weighed aliquots of 50-650 µg on a microbalance and analyzed them using the procedure outlined above. The root mean square deviation of the Fe-based mass measurement from weighed mass is ∼3% for the Ru-spike and 9-22% for the Ca-spike. This shows that the exter-

nal uncertainty of our U concentration measurements, including the effect of analytical and dissolution issues, is around 3% (1σ). Complete data and additional discussion can be found in Supplementary Material C.

2.4. Monitoring phase change with ATR-FTIR

We studied phase transitions due to laser-heating in natural hematite and goethite samples. Aliquots of several milligram of crushed material of 100-500 µm diameter (tens to hundreds of individual grains) were loaded into Pt tubes of about 3 mm diameter and 5 mm length, which were crimped at the ends. These packets were heated with the same laser heating system as described above. We prepared several aliquots of a sample and heated each packet to a temperature between 550 °C and 1450 °C. We performed experiments in both vacuum and ∼130 mbar of O_2. Samples degassed in vacuum were heated while being turbo-pumped, because the release of O_2 due to phase change would have created a much larger oxygen partial pressure than the smaller aliquots used for other heating experiments.

To establish whether reduction to magnetite occurred, we tested heated samples (still contained in Pt packets) for magnetism with a hand magnet. Pt packets were opened under a light microscope using forceps. Two individual grains were picked for dissolution and ICP-MS analysis. The rest of the heated material was powdered using mortar and pestle, which was investigated with Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy (ATR-FTIR). A spectrum from 400 to 4000 cm^{-1} was recorded with ten passes of 10 s integration time each. Phase was determined by comparing the spectra to those of synthetic hematite and magnetite powders as well as those of unheated samples. We also determined the height of peaks represen-

tative of hematite and magnetite and calculated a peak ratio. We use this ratio to estimate the amount of hematite converted to magnetite based on calibration with mixtures of synthetic hematite and magnetite (see Supplementary Material D).

Since the FTIR method can only detect a fraction of at least 5-10% magnetite in hematite, we also performed another set of experiments to constrain the onset of the hematite-magnetite phase change. We measured the release of O_2 resulting from the conversion of hematite into magnetite. Samples were laser-heated with progressively higher power, and the temperature and pressure were recorded. These experiments used a capacitance manometer, which was pumped for 24 h before the beginning of measurements. Since the laser chamber was not actively pumped during the experiment, we characterized the background rise rate several times and subtracted the background pressure from the sample measurements. After the highest temperatures were reached, the evolved gas was exposed to an LN_2 trap to determine whether the composition was mainly O_2 or whether other gases have also been released from the sample.

3. Results

3.1. Sample inhomogeneity

Undegassed hematite samples with masses of 20-800 µg show large natural variability of U, Th, and Sm concentrations as well as Th/U and Sm/U ratios (Fig. 2). We constructed kernel density estimates (KDEs) with bandwidths equal to the average 2σ-heterogeneity of 10-45 replicate analyses. We determined the median value of the distribution, which we use as a refer-

ence for judging U-loss. KDEs of measured parameters often have a single peak, although many distributions are asymmetric and skewed toward higher values. The same sample can have parameters which have a broad and asymmetric distribution, while the KDEs of other parameters are more defined. The edges of the interquartile range (IQR) of the distributions of U, Th, and Sm concentrations are between 5% of 150% from the median. U concentrations are most well-defined at around 10-20% variability, with Th and Sm concentrations both showing a variability of 20-50%. Th/U and Sm/U ratios vary about 20-40% in the IQR. Some samples have Th concentrations that are below the detection limit (MS, HM2048). These samples had Sm concentrations well above procedural blank levels and we utilized the Sm/U ratio instead of the Th/U ratio to detect U-loss.

Each set of replicates contains several outliers, almost exclusively of higher than average U, Th, or Sm concentrations (Fig. 2). Inhomogeneity in U, Th, and Sm concentrations increases with smaller sample mass (Fig. 3), and concentrations of aliquots >500 µg are close to the bulk values.

Goethite samples have a larger natural variability in U, Th, and Sm concentrations (Fig. 4). Samples CIT and RH have defined peaks of U and Th concentration, similar to most of hematite samples. Samples YAN, blade, and Lyp did not show a defined peak of U or Th concentrations, but a broad distribution of values with multiple peaks. Due to their great natural variability, samples blade and YAN were not used for heating experiments, but they were analyzed for phase changes using ATR-FTIR.

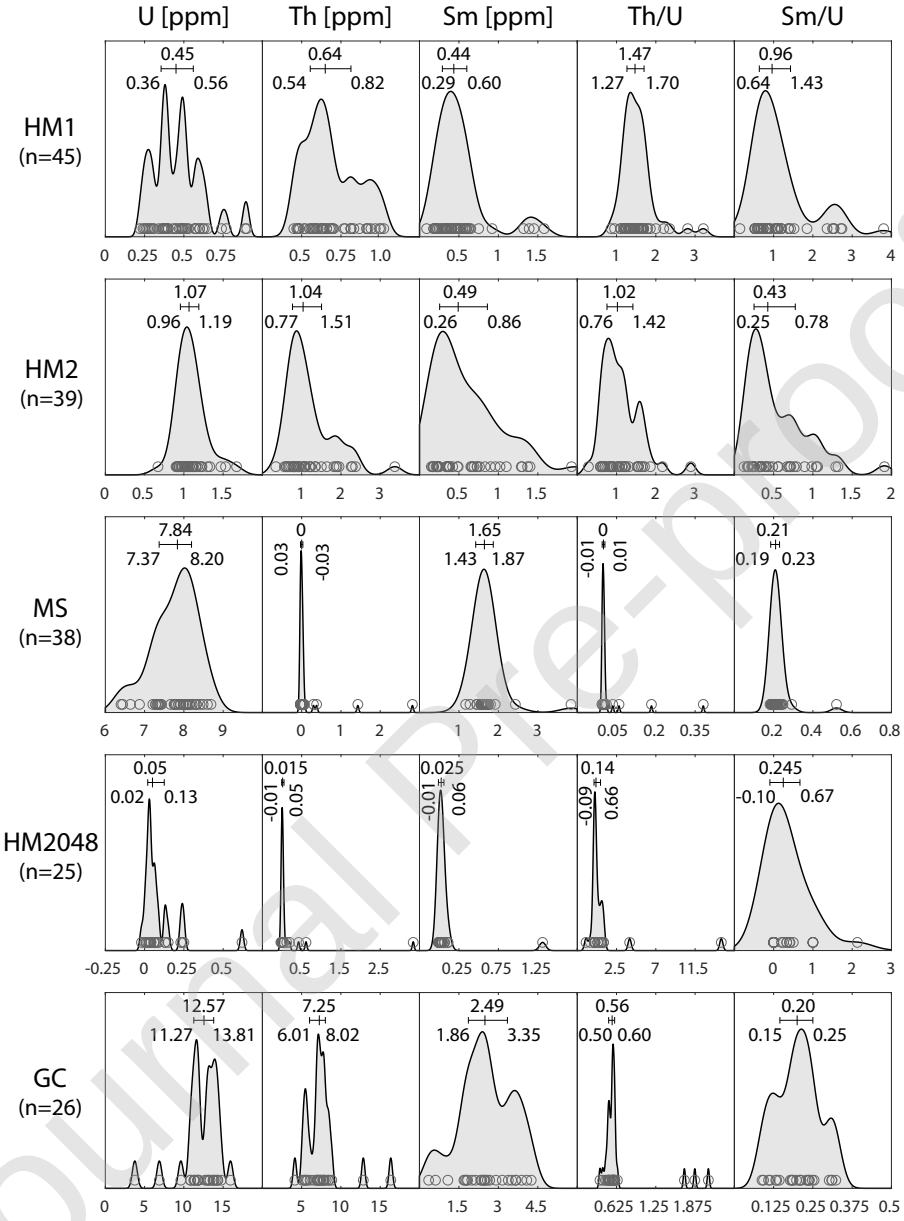

Figure 2: Concentrations of U, Th, and Sm of undegassed hematite samples measured on 25-45 aliquots of 20-800 µg, as well as Th/U and Sm/U ratios. Given are KDEs with bandwidths of the average 2σ heterogeneity of individual measurements. Bars above the KDEs indicate the median value and the interquartile range.

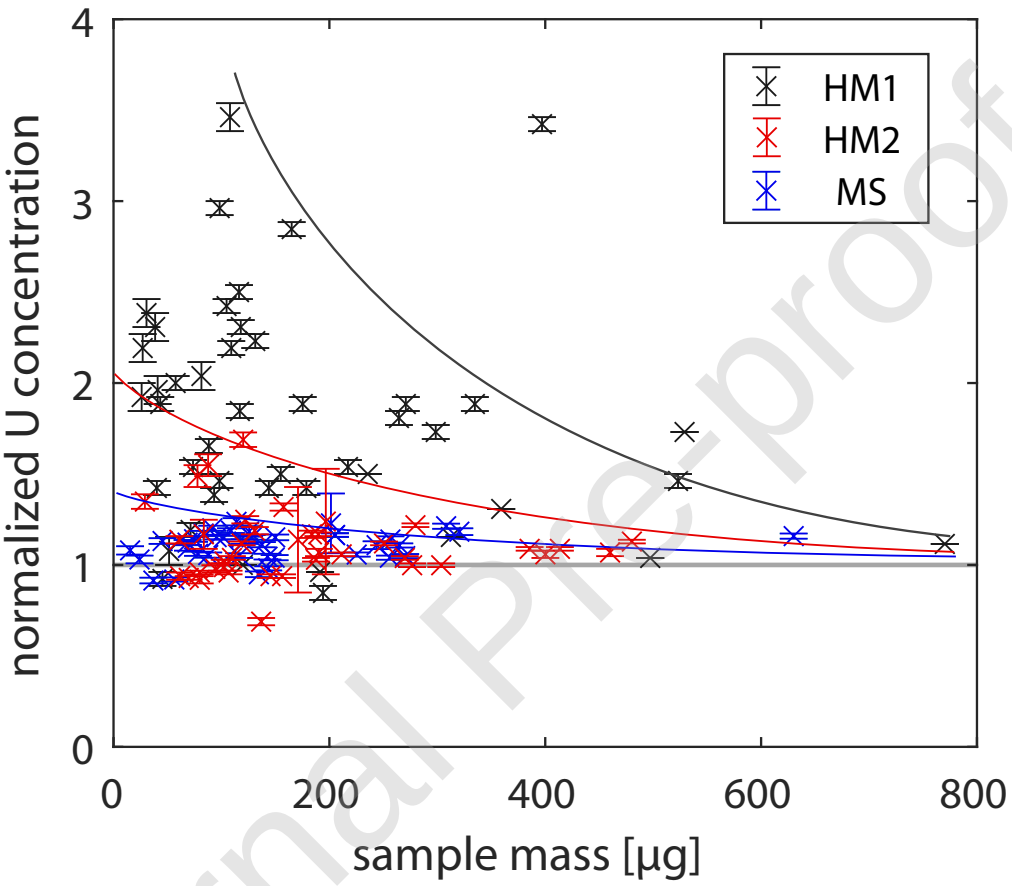

Figure 3: Inhomogeneity of U concentration in three samples by mass of aliquot. Lines show general trends for different samples. Gray line at 1 represents the bulk measurement. U concentrations were normalized by bulk concentrations measured on several milligrams of sample material. Small masses have larger variability, while larger aliquots have U concentrations close to the bulk value.

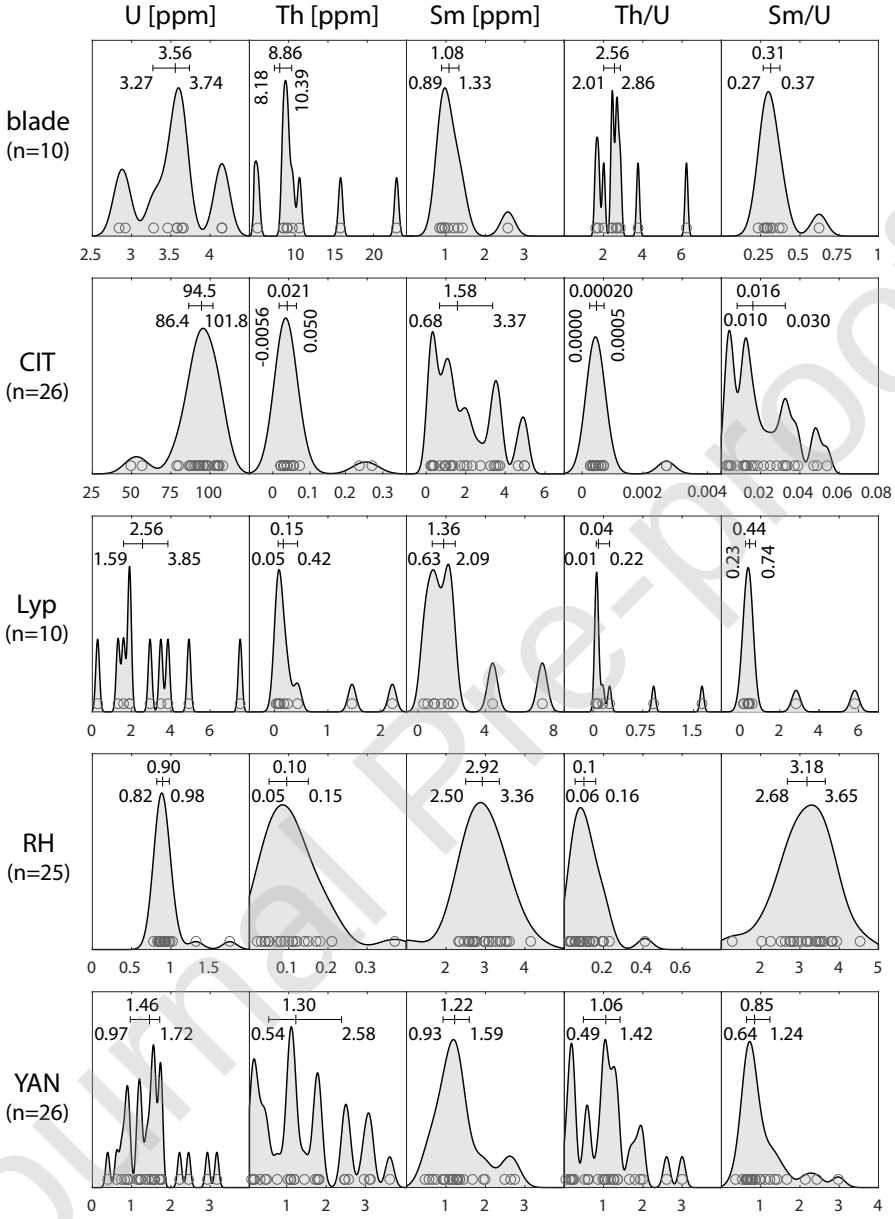

Figure 4: Concentrations of U, Th, and Sm of undegassed goethite samples measured on 10-26 aliquots of 20-350 µg, as well as Th/U and Sm/U ratios. Given are KDEs with bandwidths of the average 2σ heterogeneity of individual measurements. Bars above the KDEs indicate the median value and the interquartile range.

3.2. U-loss in vacuum heating

We heated aliquots of four hematite (n=197) and four goethite samples (n=41) to temperatures between 500 °C and 1400 °C under vacuum. Measured values of U, Th, and Sm concentrations as well Th/U and Sm/U ratios were normalized by the median value of undegassed aliquots or the average values measured by two-aliquot bulk analyses to show a summary of the results (see Fig. 5). Plots and data for each individual hematite and goethite sample, separated by vacuum and O_2 experiments as well as by whether Pt or Nb tubes were used, can be found in Supplementary Material E.

Aliquots of the same sample heated to different temperatures showed the first signs of U-loss at ∼980 °C for both hematite and goethite (Fig. 5). There is considerable scatter of all measured parameters due to natural variability of the samples in U, Th, and Sm concentrations. However, clear trends emerge with a large number of aliquots of the same sample. U-loss manifests as a decrease in U concentration with a resultant increase in Th/U or Sm/U ratio. The amount of U-loss at any specific temperature above 980 °C varies between 5% and >95% and is not reproducible, due to a combination of natural parent isotope heterogeneity and sample response. We observed no systematic loss of either Th or Sm at high temperatures. Some samples had Th concentrations that were below the detection limit. For these samples, we utilized the Sm/U ratio, which showed the same increase due to U-loss as the Th/U ratio. The Th/U or Sm/U ratios are indicative of major U-loss. The natural variability of these parameters is 20-50% of the median value, therefore U-loss in individual samples was only apparent when it deviates by at least this amount. The Th/U or Sm/U ratio rapidly increases within a

narrow temperature range of 50-100 °C from the point of initial U-loss (Fig. 5). We found no difference in the U-loss temperature or amount of U-loss between Pt packets and Nb packets (for data see Supplementary Material E).

The amount of helium extracted from the sample is a function of both temperature and heating time. For the same temperature, aliquots which have been heated for longer show a larger fraction of total helium extracted than those heated for shorter periods of time. Helium is extracted at a different rate for each sample, reflecting differences in retentivity. Some samples have He concentrations higher than those measured on bulk material, most likely due to U and Th concentrations in the aliquot which are higher than the bulk values.

Hematite sample MS as well as all goethite samples are fully outgassed at around 800 °C (Fig. 5). In hematite samples HM1 and HM2, which are highly retentive, helium is fully extracted at ∼1150 °C and ∼1250 °C, respectively. Therefore, in these samples, helium is not fully extracted below the temperature of U-loss. Apparent ages are below the bulk age up to the U-loss temperature, then they increase rapidly as U is lost and more helium is extracted. The apparent ages at high temperatures are higher than the bulk age, quickly rising to several billions of years. For these samples, there is no age plateau and standard approaches cannot be used to accurately date the sample. An increase of several hundred degrees without U-loss is required to make these samples datable by the single-aliquot (U-Th)/He method.

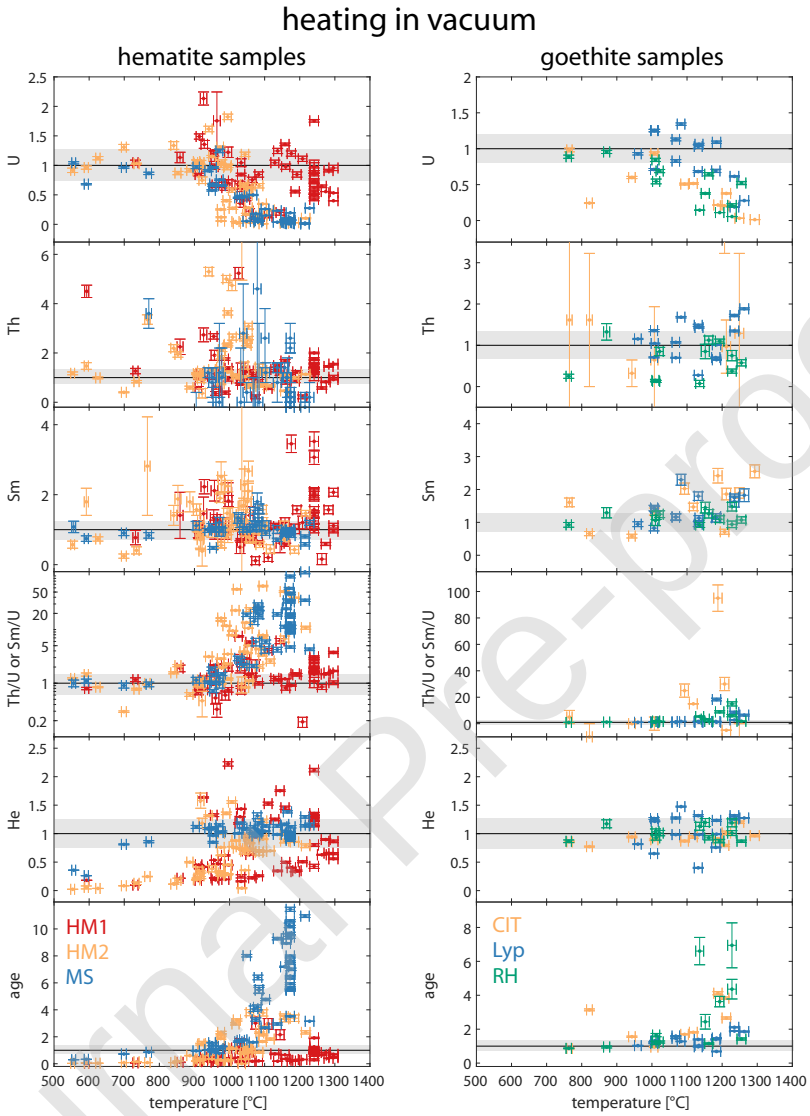

Figure 5: Hematite and goethite samples heated to temperature between 500 and 1300 °C in vacuum. All values were normalized by median value from undegassed aliquots (U, Th, Sm, Th/U or Sm/U; see Figs. 2 and 4) or two-aliquot bulk analyses (age, He concentration; see Tab. 1) and gray areas represent the typical range of values. U-loss is apparent as a deviation from the typical range of values in U concentration, Th/U or Sm/U ratio, and age. U in both hematite and goethite is lost at temperatures above ~980 °C.

3.3. Effect of heating time

Since the extraction of helium occurs by diffusion, prolonged heating time at a lower temperature can be substituted for high temperatures to completely extract helium. To test whether U-loss occurs at lower, 'safe' degassing temperatures, we performed experiments in which samples were heated to 950 °C in vacuum for various lengths of time between 5 min and 4 h. U-loss was detectable at isothermal holding times over 20 min (Fig. 6). U-loss increased with holding time, with almost complete U-loss occurring at around 4 h. The same trend can be seen in an increase of both the Sm/U ratio and the apparent age. Partial U-loss occurs at temperatures below those of massive U-loss, but only becomes apparent at long holding times. Therefore, longer holding times at lower temperatures are not a solution to the problem of U-loss in hematite and goethite for vacuum-heating experiments.

3.4. Phase transition during heating

We acquired ATR-FTIR spectra of samples heated to temperatures between 500 °C and 1350 °C to investigate phase change due to laser-heating in vacuum and O_2. The dominant phase was interpreted by comparing spectra of samples to those of synthetic goethite, hematite, and magnetite powders of 0.15-0.35 µm grain-size. An example of a series of ATR-FTIR analyses is shown for sample HM2 (Fig. 7). We performed similar analyses on a total of five hematite samples and three goethite samples, the full results of which can be found in Supplementary Material D.

We observed partial conversion of hematite to magnetite in vacuum starting at around 950-990 °C (Fig. 9). Minor U-loss, measured on the same material was detected in the same temperature range. Complete conversion

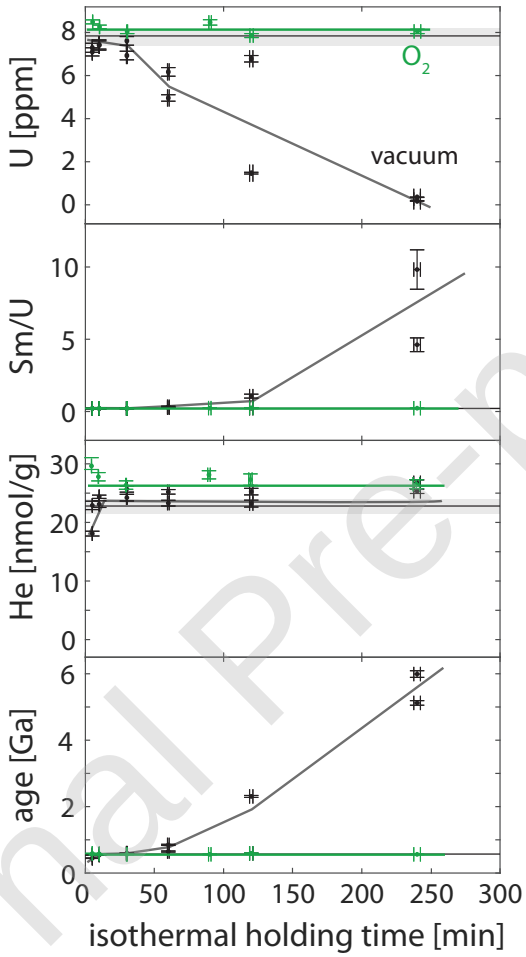

Figure 6: Effect of heating time on hematite sample MS with isothermal holding in vacuum at 950 °C (black). At this temperature, U-loss in vacuum is detectable for heating times >20 min. Samples heated in ~130 mbar O_2 at 1000 °C (green) do not show any loss of U regardless of heating time. Black and green lines represent general trends.

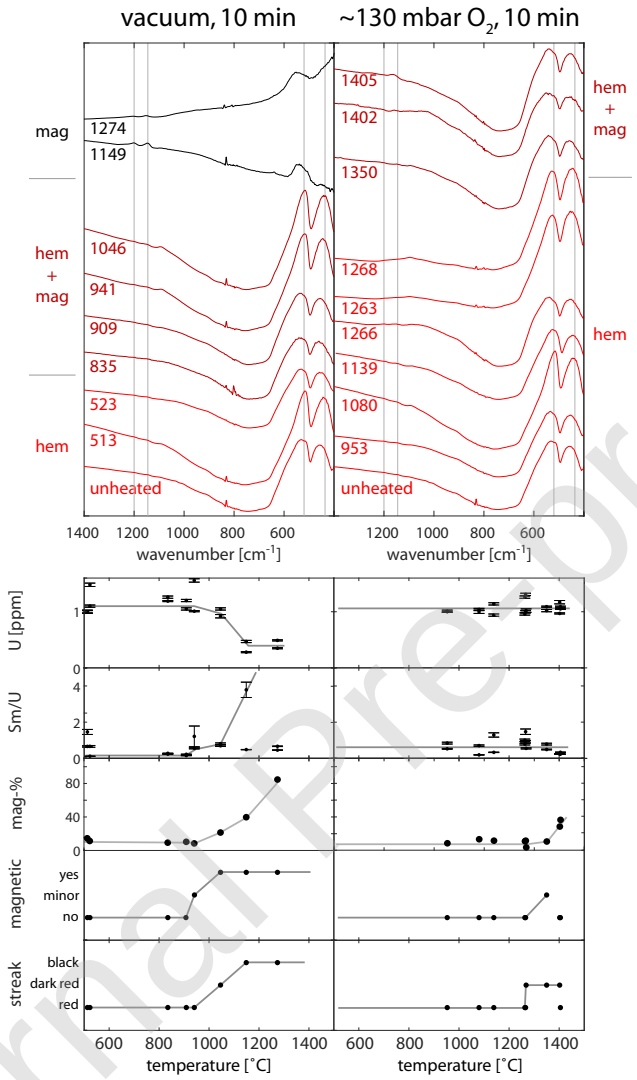

Figure 7: ATR-FTIR spectra of hematite sample HM2, heated to different temperatures (given in ˚C) in vacuum and in 130 mbar of O_2 for 10 min. Phases are indicated next to spectra. U concentrations and Sm/U ratios were measured on subsamples of the same material used for ATR-FTIR. Estimated magnetite percentage (mag-%) was determined from peak ratio. Initiation of U-loss occurs at the same temperatures as detectable partial conversion of hematite to magnetite. Partial conversion of sample material to magnetite is detectable with a hand magnet and by streak color.

of hematite to magnetite occurred between 1050 °C and 1200 °C, associated with major loss of U. This pattern of U-loss is similar to that found in vacuum heating experiments described above. The samples that contained detectable amounts of magnetite were found to respond to a weak hand magnet while still in their Pt packets. The streak of the sample, when powdered, showed progressive darkening (3/6 10R to 2.5/1 10R) as a result of the increasing amounts of magnetite relative to hematite at high temperatures.

Samples heated in pure O_2 with a $p(O_2)$ of ∼130 mbar for 10 min or 60 min showed a conversion of hematite to magnetite at higher temperatures than in vacuum (Fig. 7), as predicted by the phase diagram of Ketteler et al. (2001) (Fig. 8). Partial conversion of hematite to magnetite was observed between 1250 °C and 1350 °C. Conversion of about 40% of the sample to magnetite was observed at the highest temperatures studied here (∼1400 °C). This demonstrates that the phase transition starts when the temperatures cross the predicted phase boundary. However, presumably due to kinetic effects, the samples are only partially converted from hematite to magnetite and much higher temperatures are required to fully convert samples to magnetite within the time-frame of the experiments.

Similar patterns were found for goethite, although conversion to magnetite and U concentration differ more among samples. Goethite samples heated in vacuum were present as hematite at the lowest temperatures studied here (∼550 °C), with no evidence of remnant OH-groups. The first conversion of hematite to magnetite in goethite samples was observed at around 950 °C. Massive U-loss occurs around 1000-1050 °C, associated with a rapid increase in the magnetite fraction. Full conversion of hematite to magnetite

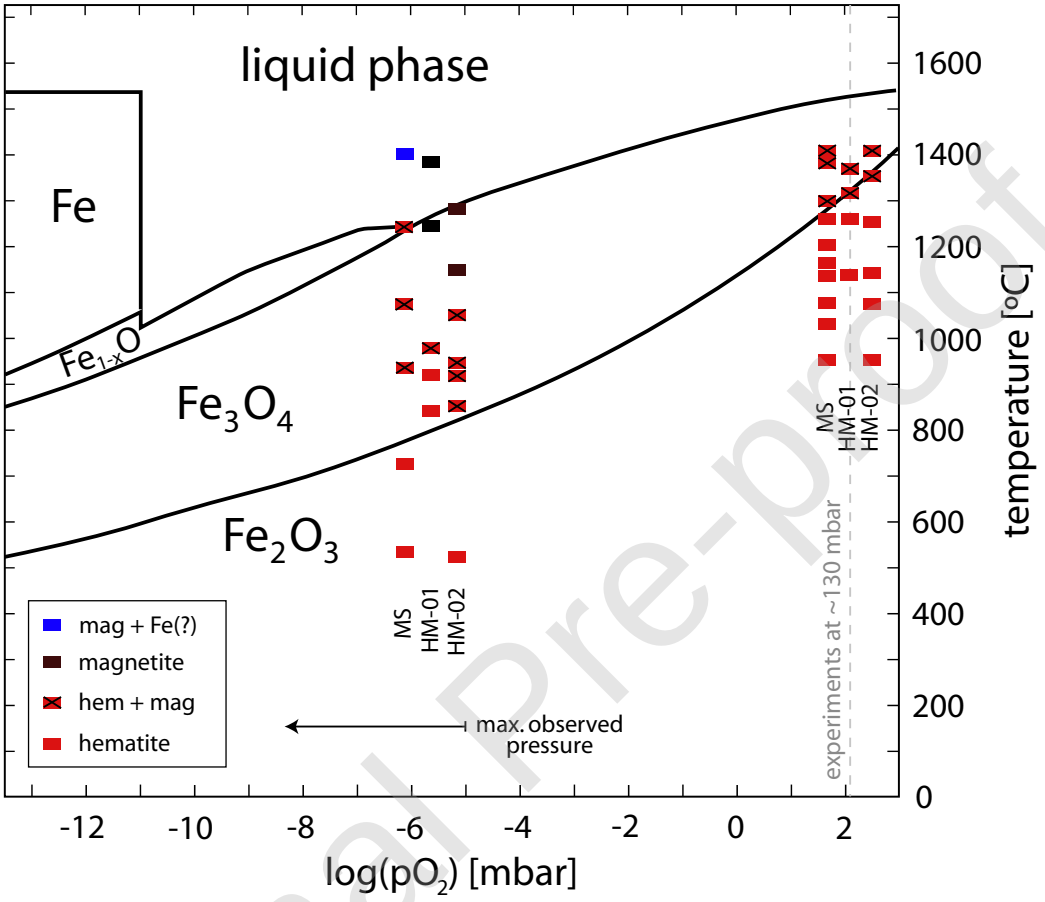

Figure 8: Theoretical equilibrium phase diagram (redrawn after Ketteler et al., 2001) with phase determinations of three different hematite samples determined by ATR-FTIR. The exact oxygen partial pressure (pO_2) of samples heated in vacuum is unknown, but lower than the maximum observed pressure of 10^{-5} mbar. Experiments in O_2 were performed at ~130 mbar. Our observations show that partial conversion of hematite to magnetite occurs at the predicted phase transition temperature, which confirms the phase diagram, but demonstrate that full conversion of hematite to magnetite is kinetically inhibited to higher temperatures than the equilibrium phase transition temperature.

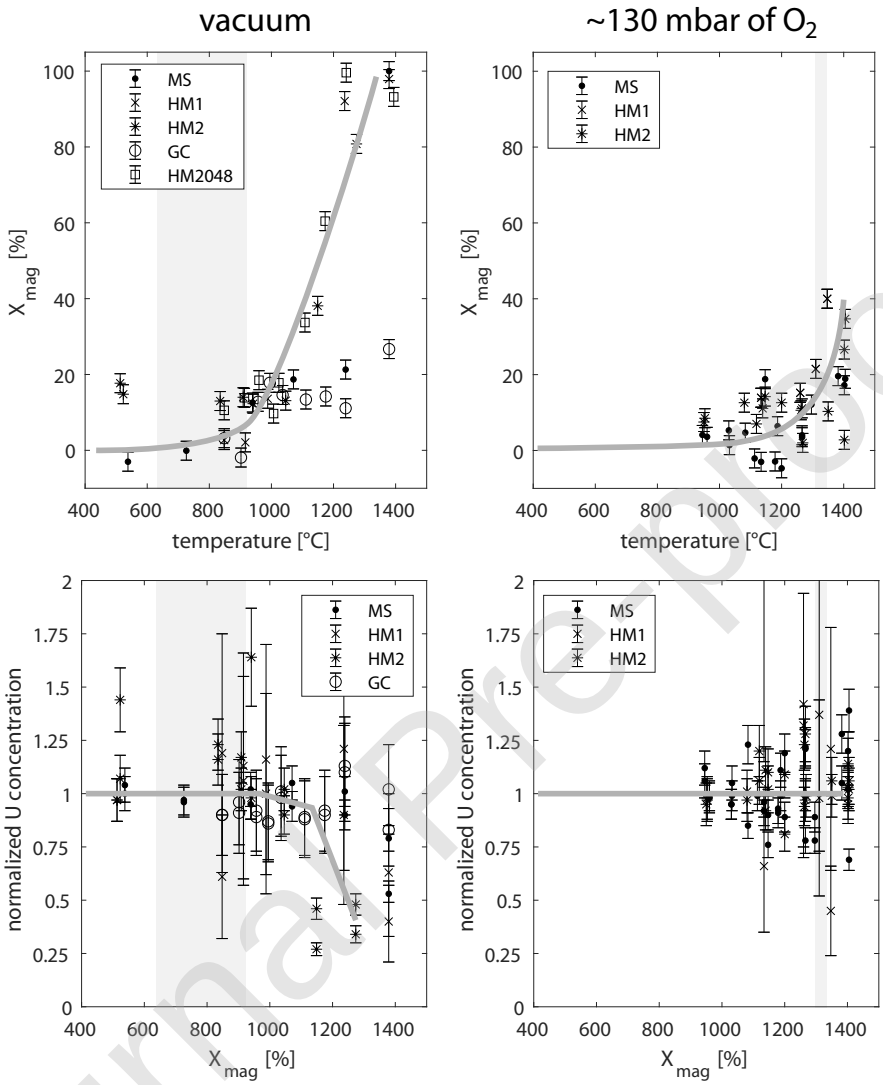

Figure 9: Summary of all hematite ATR-FTIR experiments. Magnetite percentage (top) and U concentration (bottom) as a function of temperature for heating of samples in vacuum (left) and 130 mbar of O_2 (right). U concentrations are normalized by the median value of undegassed aliquots. Massive U-loss correlates with major conversion of hematite to magnetite. Shaded region is temperature range of hematite-magnetite transition from phase diagram of Ketteler et al. (2001) based on measured and estimated oxygen partial pressures. Gray lines show general trend.

occurs at around 1300 °C, above which all goethite samples showed ATR-FTIR spectra that were almost flat, which we interpret as decomposition of magnetite to elemental iron. This was not observed in any hematite samples heated to similar temperatures.

Based on the ATR-FTIR spectra, goethite samples heated in O_2 are mainly hematite at the lowest observed temperatures (∼900 °C), but there is evidence of remnant OH-groups up to 1400 °C. The first conversion of hematite to magnetite in goethite samples was observed at around 1050 °C, implying that hematite derived from dehydroxylation of samples originally present as goethite is thermodynamically and kinetically different from hematite samples. Major U-loss in goethite samples heated in O_2 coincides with a rapid increase in magnetite fraction at around 1200 °C.

3.5. Phase transition from oxygen release

With ATR-FTIR, identification of hematite-magnetite phase transition was only possible for more than 5% conversion. In order to identify whether there is conversion of hematite to magnetite at temperatures below ∼980 °C in vacuum, we laser-heated samples and monitored pressure build-up due to release of O_2 from the sample with a capacitance manometer. The lower limit of the pyrometer is about 550 °C, and therefore samples were heated to this temperature or above on the first heating step.

We observed a minor pressure increase of 1-3% of the final pressure at temperatures below 550 °C (Fig. 10), which stays constant up to about 800-900 °C. This is presumably due to outgassing of volatiles, such as CO_2, N_2, or H_2O contained in the sample. A significant amount of gas evolved at temperatures >800 °C, suggesting the first release of O_2 due to phase change from

hematite to magnetite. Pressure increased rapidly between 1000 °C and 1300 °C, with the largest increase around 1150 °C. Above ~1300 °C there is only minor change in pressure, which suggests that most of the hematite has transformed to magnetite. The final pressure was about 10^{-2} mbar, which is consistent with the amount of O_2 (10^{-7} mol from ~20 µg of hematite sample) released into the volume of the laser chamber and tubing ($\sim 5 \cdot 10^{-4}$ m^3) due to complete conversion of hematite to magnetite (release of 0.5 mol of O_2 per mole of hematite). After the experiment, we exposed the gas to a charcoal trap cooled with liquid nitrogen, which led to a reduction of 95-99% of the total pressure. This is consistent with most of the gas being O_2, since only CH_4, H_2, Ne, and He would not condense. The contribution from He and Ne is $<10^{-7}$ mbar.

3.6. Samples heated in oxygen

Since we have shown that U-loss correlates with phase change from hematite to magnetite, we used an increased $p(O_2)$ during laser-heating to raise the phase transition temperature (Ketteler et al., 2001) to test whether this will prevent U-loss at high temperatures. In hematite, the initiation of U-loss occurred at 1180-1200 °C in the presence of O_2, with massive U-loss of up to 99% between 1200 °C and ~1400 °C (Fig. 11). U-loss increases with both temperature and heating time. U-loss is apparent in both U concentrations and Th/U or Sm/U ratios. As in vacuum, we observed no systematic loss of either Th or Sm at high temperatures.

At holding times of 10-30 min, helium in sample MS was extracted at ~1000 °C. Samples HM1 and HM2 were completely outgassed at 1250 °C and 1350 °C. The apparent age is close to the two-aliquot age for samples MS and HM2

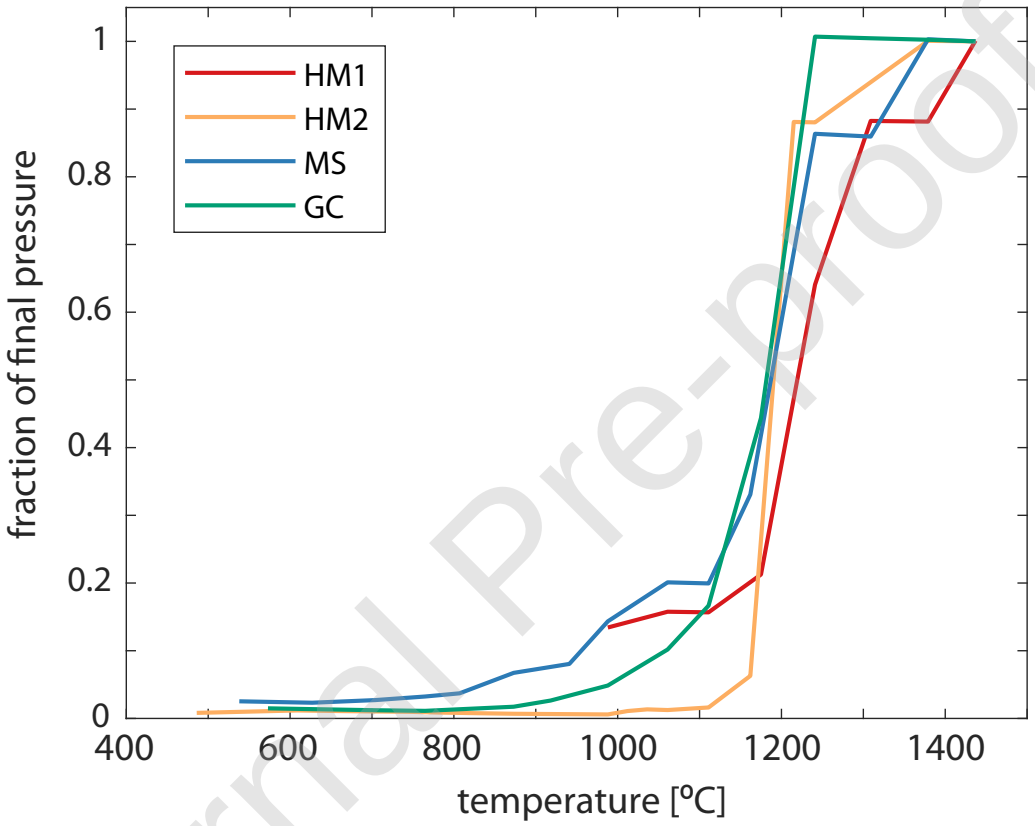

Figure 10: Pressure in the laser chamber as a function of temperature, interpreted to result from release of oxygen from hematite during transition. Measurements were normalized by the maximum observed pressure to compare samples of different mass.

and increases exponentially for temperatures >1300 °C. In sample HM1, the apparent age remains below the two-aliquot bulk age at temperatures above which massive U-loss occurred, and helium could not be fully extracted even at heating times of several hours. Some aliquots of this sample show clear U-loss of 20-50%, yet the apparent ages are still below two-aliquot age since less than 50% of the total helium was extracted. Aliquots of sample MS heated to a temperature of 1000 °C for holding times between 5 min and 4 h show no signs of U-loss (Fig. 6). This demonstrates that samples can be held for long periods of time below the U-loss temperature in O_2, which is not possible in vacuum.

In goethite, the initiation of U-loss is raised to ∼1100 °C (Fig. 11). Helium is fully extracted from all goethite samples even at 800 °C and the apparent ages are within uncertainty of previously determined ages. Progressive U-loss occurs between 1100 °C and 1300 °C, as indicated by decrease in U concentration and concurrent increase in Th/U or Sm/U ratio.

4. Discussion

U-loss as a result of heating is a concern in single-aliquot (U-Th)/He geochronology and thermochronology of hematite and goethite, because it can lead to incorrect ages. The aim of this study was to find ideal extraction conditions, at which single-aliquot dating of hematite is possible. U-loss has been studied in one goethite sample by Vasconcelos et al. (2013), who found a plateau of 'safe' degassing temperatures between the points of complete extraction of helium and the onset of U-loss. Reiners et al. (2014) reports decomposition of sample material and flowage out of the enclosing tube at

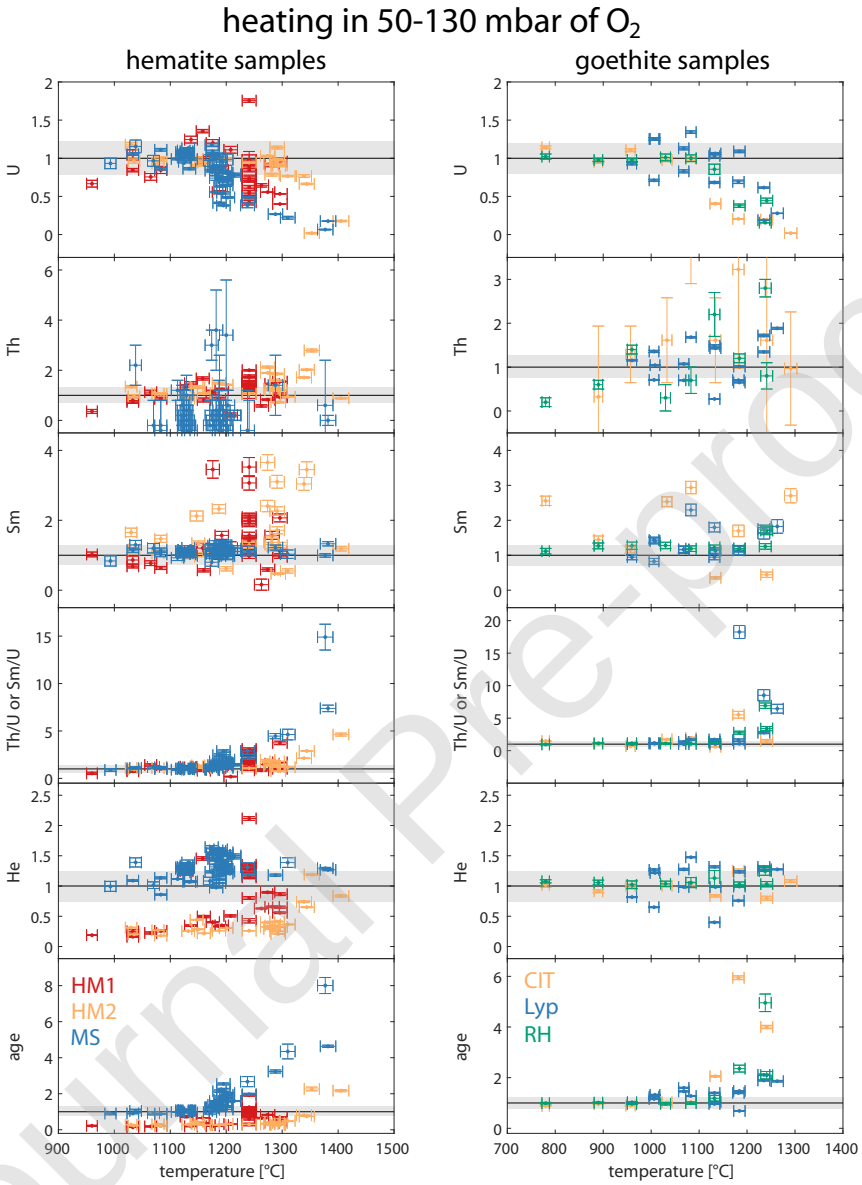

Figure 11: Hematite and goethite samples heated in 50-130 mbar of O_2. All values were normalized by median value from undegassed aliquots (U, Th, Sm, Th/U or Sm/U) or two-aliquot bulk analyses (age, He concentration) and gray areas represent the typical range of values. U-loss temperature for is deferred to 1180 °C for hematite and to ∼1100 °C for goethite, compared to ∼980 °C for heating in vacuum.

temperatures >850 °C. Garcia et al. (2018) even report volatilization of Fe, Mn, and other elements in iron- and manganese-oxides at high temperatures. We have also observed deposits on the planchet due to volatilization of Fe from a sample out of Pt packets which were open at the sides. This suggests that the oxidation of hematite to magnetite can lead to significant restructuring of the sample material and mass loss from the packet.

Several studies have lowered extraction temperatures for both goethite and hematite to 500-850 °C because U volatilization was observed at temperatures above 1000 °C (Danišík et al., 2013; Reiners et al., 2014; Garcia et al., 2018; Wells et al., 2019). For very fine-grained hematite samples, which likely have low helium-retentivity, these temperatures might be sufficient to completely extract helium. Re-extracts are one approach to test for complete helium extraction. In some samples, there might be highly retentive domains which require much higher temperatures to extract significant amounts of helium, which we observed in sample HM1. Complete helium extraction in such samples can only be assured by degassing a previously heated sample to temperatures close to fusion, which leads to loss of the sample. This is a way to test complete helium extraction if there is a large amount of homogeneous sample material, but might not be feasible if the sample material is severely limited or displays large inhomogeneity in domain size.

The use of an 'evaporation correction' for U concentrations in samples, which were heated to temperatures at which they experience U-loss, was suggested by van den Kerkhof et al. (2018). This is essentially a two-aliquot approach. However, we have shown that U concentrations in undegassed samples can be highly variable, especially at the scale of tens to hundreds of micrograms,

which is typical size of single-aliquot samples. In addition, the amount of absolute U-loss is not reproducible between aliquots. This suggests that any 'evaporation correction' would carry an uncertainty of at least 20-50% and is therefore not a feasible way of obtaining precise and reproducible (U-Th)/He ages. Partial U-loss of homogeneous material produces age-eU correlations, in which low U concentrations are associated with high age, and vice versa. Another possibility for completely extracting helium from a sample is to hold them for longer periods of time at lower temperatures. Due to the logarithmic nature of thermally activated Fickian diffusion of helium through the crystal, isothermal holding times increase manyfold from even a slight reduction in temperature (Fig. 12). Conversely, any small temperature increase without U-loss leads to a considerable reduction in the required heating time. We found that heating samples at a temperature ∼950 °C, which was previously assumed to be 'safe' for iron-oxide outgassing (Vasconcelos et al., 2013) resulted in massive U-loss at total heating times over 20 min (Fig. 6). Complete extraction of helium from a highly retentive sample at temperatures below 950 °C would require much longer heating times. While longer holding times facilitate greater helium extraction, they simultaneously promote greater U-loss in vacuum.

4.1. Phase transition and U-loss

In experiments in which we heated aliquots of hematite and goethite samples to different temperature in vacuum, we found that U-loss first occurs at 980-1000 °C (Fig. 5), as evidenced by a decrease in U concentrations and increased Th/U and Sm/U ratios. This is the same temperature range as was observed for goethite and hematite in previous studies (Vasconcelos et al.,

2013; Danišík et al., 2013; Reiners et al., 2014). Hematite samples showed a more consistent U-loss temperature than goethite samples. This difference could be due to the nature of samples, or it might be because of the larger natural variability of U, Th, and Sm concentrations in the goethite samples studied here, which make U-loss harder to detect.

The phase diagram of Ketteler et al. (2001) predicts the phase transition from hematite to magnetite at equilibrium conditions to occur at 850 °C and 710 °C at a $p(O_2)$ of 10^{-5} mbar and 10^{-8} mbar, respectively (Fig. 8). This suggests that an 'age plateau' up to 950 °C for goethite, as described by Vasconcelos et al. (2013), is allowed only by kinetics. Pressure in the laser chamber before degassing is about 10^{-8} mbar. The highest pressures observed during degassing are around 10^{-5} mbar. This can be taken as an upper bound for the possible oxygen partial pressure in the laser chamber during vacuum degassing. Since oxygen is being released by the sample as hematite transforms to magnetite, the $p(O_2)$ in the laser chamber might increase and lead to a higher hematite-magnetite transition temperature for the remaining material. This negative feedback process can cause an increase in the actual phase transition temperature compared to that at initial vacuum conditions. At Caltech, samples are usually degassed while exposed to a charcoal trap cooled with liquid nitrogen, which traps most gases evolved from the sample.

We investigated the phase change from hematite to magnetite in samples initially present as hematite and goethite using ATR-FTIR. The first detectable conversion of hematite to magnetite in these samples was observed at temperatures of 950-990 °C, which coincides with the inception of U-loss measured

on aliquots of the same material used for ATR-FTIR analyses. There was more scatter of U concentrations of aliquots which had experienced U-loss in ATR-FTIR experiments than was observed in heating experiments. Each packet heated for ATR-FTIR samples contained tens of milligrams of sample material aggregated from tens to hundreds of individual grains, whereas the much smaller packets for single-aliquot analyses contained only a single fragment of sample with masses of 10-100 µg. U volatilized from the outside of any individual grain might condense onto the neighboring grain with a large amount of sample material present, and consequently the aliquot might appear to have experienced a smaller amount of U-loss. With only a single grain present in a small packet, U volatilized from the sample might be absorbed by the packet or escape through the ends of the tube and is not quantitatively recoverable.

Goethite samples were observed to convert more readily from hematite to magnetite. We also observed a possible decomposition of magnetite to elemental iron in these samples, which is predicted by a published phase diagram (Fig. 8), but was not observed in hematite samples heated to comparable temperatures. Since goethite samples used in this study are more fine-grained than hematite samples, this might be evidence of grain-size dependent kinetics of the phase transition. The dehydroxylation reaction that transforms goethite to hematite at 180-300 °C (Prasad et al., 2006; Ruan et al., 2001) can also lead to major re-crystallization of the sample, with a possible further reduction of grain-size. This might influence the kinetics of the hematite-magnetite transition at higher temperatures, which could contribute to cause the phase transition and U-loss to happen at temperatures

lower than those for hematite. The goethite-hematite transformation temperature is affected by the amount of Al-substitution for Fe (Cornell and Schwertmann, 2003). We are not aware of any published works on the effect of Al-substitution on the hematite-magnetite transition. None of the samples studied here had any significant amounts of Al-substitution, so we cannot exclude effects on the hematite-magnetite transition temperature and associated U-loss.

We interpret the correlation between phase transition temperature and U-loss as evidence that these processes are connected. The phase transition of hematite to magnetite causes a major re-organization of the crystal structure as Fe^{3+} is reduced to Fe^{2+}. The coordination of Fe changes from octahedral coordination to a spinel structure and oxygen is released from the crystal. This seems to lead to a major fractionation of U, with Th and Sm being quantitatively retained, while almost none of the U is incorporated into the magnetite. U incorporated in hematite likely substitutes for Fe in octahedral configuration (Ilton et al., 2012) and might be reduced if it cannot attain this configuration for steric reasons (Skomurski et al., 2011). Unlike Th and Sm, U is redox-sensitive and incorporation of U into iron-oxides also depends on the Fe^{2+} density (Skomurski et al., 2011). The fractionation of U relative to Th and Sm during the hematite-magnetite transition is therefore likely a result of the change in oxidation state of Fe and the re-organization of the crystal structure. If U is not incorporated into the magnetite crystal structure during re-crystallization, it might be brought to the surface of the crystallite, where it could evaporate and be ejected from the packet.

We observed no major loss of U as a result of the goethite-hematite transition,

as evidenced by U concentrations of samples heated between 800 °C and 980 °C being close to those of undegassed aliquots (Fig. 5). This transition involves only dehydroxylation of inter-layer -OH groups and the oxidation state of Fe does not change. Fractionation due to differences in redox-sensitivity is therefore not expected for this reaction. Due to the natural variability of undegassed samples, we cannot exclude minor amounts of U-loss associated with this process. However, some goethite samples have previously given very reproducible ages when degassed at 900-950 °C (e.g. Vasconcelos et al., 2013), so we do not expect any U-loss due to the goethite-hematite transition of samples during laser-heating.

Since our results indicated that U-loss in iron-oxides might be caused by the phase transition from hematite to magnetite, we investigated ways to raise the phase transition temperature. In ATR-FTIR experiments, we observed that the phase transition temperature of hematite samples was raised to about 1250 °C due to the presence of ∼130 mbar of O_2 (Fig. 9).

We observed no U-loss in samples heated in O_2 for ATR-FTIR analyses. Laser-heating experiments of aliquots in comparable oxygen pressures similarly showed that U-loss was initiated at around 1180 °C in hematite samples and 1100 °C in goethite samples. This demonstrates that deferring the hematite-magnetite transition to higher temperatures has affected the temperature at which U-loss occurs, which provides further evidence that U-loss is caused by the phase transition from hematite to magnetite. This information can be used to raise the phase transition temperature, and therefore the U-loss temperature, as required by the sample. According to the phase diagram of Ketteler et al. (2001), oxygen partial pressures of 1 mbar, 10 mbar,

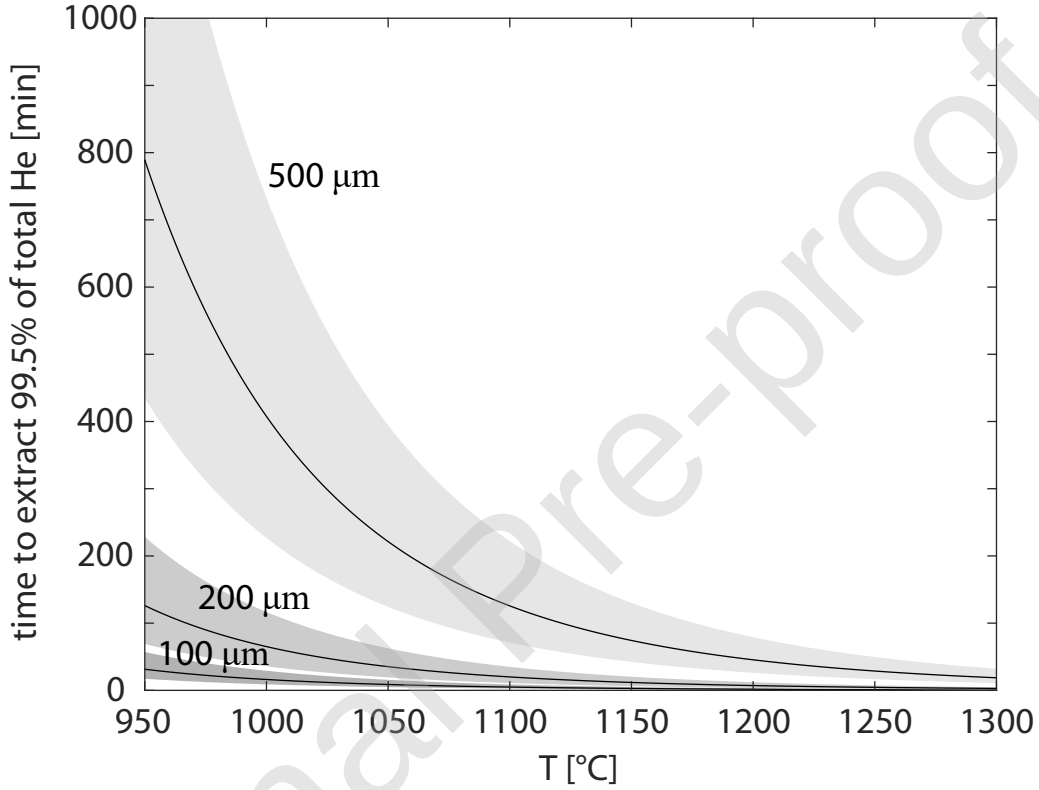

Figure 12: Modeled time to extract 99.5% of total amount of helium for different domain sizes using the hematite diffusion coefficients of Farley (2018). Gray areas represent 2σ uncertainty. Safe limit of vacuum degassing of hematite is around 950 °C. Degassing in ∼130 mbar of O_2 can be done safely without U-loss up to ∼1150 °C in hematite. We assume that presence of O_2 does not affect the helium release rate.

and 100 mbar can raise the hematite-magnetite transition to about 1120 °C, 1210 °C, and 1310 °C. We have found minor amounts of magnetite up to 100 °C below these temperatures, suggesting that modeled T-p(O_2) conditions can deviate from theoretical predictions in natural samples.

4.2. Implementation of high p(O_2) method

The normal setup for (U-Th)/He laser heating was amended for heating samples in a pure O_2 atmosphere. A manifold with an O_2 tank, a cold finger, and a manometer was connected between the laser chamber and the line (Fig. 13). We filled the tank with O_2 to a pressure of 22 psi (152 kPa). After pumping the laser chamber to $<10^{-8}$ mbar and confirming a ^{4}He blank of <0.001 ncc, O_2 was released into the laser chamber with a pipette that delivers about 130 mbar per draw. Oxygen pressure was measured using a manometer. The O_2 was then fixed on a cold finger cooled with LN_2, and this was turbo-pumped for 1 h to remove any helium impurities in the O_2.

Before a measurement, the laser chamber is ion-pumped for 20 min. The laser chamber was closed to the U-trap at valve A (Fig. 13) and O_2 was released into the laser chamber by removing the LN_2 dewar from the cold finger with an automated lifter mechanism. The aliquot was then heated using a diode laser controlled by a PID system with feedback from an optical pyrometer. The required laser output power for heating samples in O_2 was a factor of five to ten larger than for samples heated to the same temperatures in vacuum, due to the higher attenuation of the laser beam in O_2 as well as increased convective loss of heat from the packet.

We did not heat samples to setpoints within less than 50 °C below the actual phase transition temperatures to allow for minor temperature overshoots and

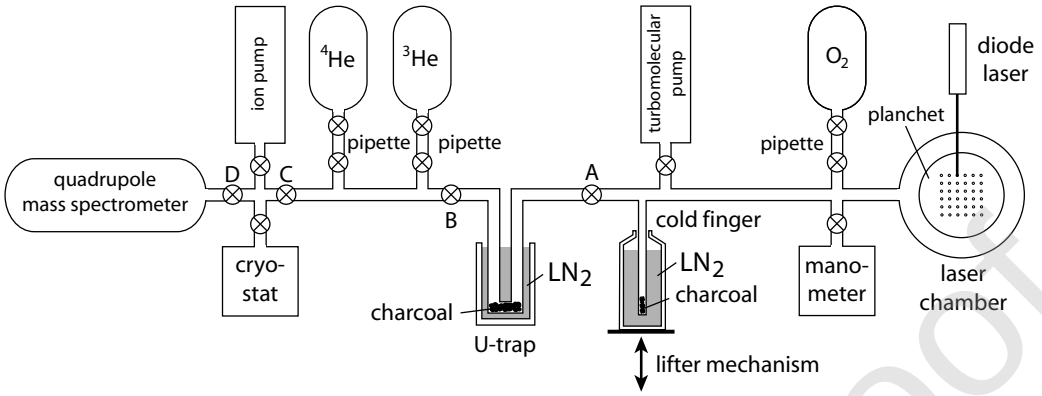

Figure 13: Schematic diagram of the vacuum line used for O_2 degassing. A calibrated amount of O_2 is released into the laser chamber from the O_2 tank using a pipette. The lifter mechanism can be used to release and capture O_2 on the cold finger before and after laser heating. Samples are degassed with 130 mbar of O_2 present, which is completely trapped before mass spectrometric analysis.

inhomogeneity within the Pt packet as well as sample-dependent differences in transition temperature. We have observed minor U-loss for long holding times at around 1200 °C, which should be taken as the maximum allowable temperature for degassing of hematites in 130 mbar of oxygen partial pressure.

After degassing, the LN_2 dewar is moved back onto the cold finger and the O_2 is again captured on the activated charcoal. The helium evolved from the sample is mixed with a controlled amount of ^{3}He spike. The gas passes through a U-trap filled with activated charcoal and cooled by LN_2, which helps to capture any remaining O_2 in the line and prevents it from reaching the cryogenic pump or the mass spectrometer. Helium is then adsorbed onto activated charcoal on a cryogenic pump at 14 K and released into the mass spectrometer at 36 K.

We initially performed some experiments using Nb packets, which have been used for many past studies (e.g. Evenson et al., 2014; Calzolari et al., 2018; Garcia et al., 2018; McDermott et al., 2017). We found that Nb turned dark within seconds of heating in an O_2-rich atmosphere, associated also with a drop in oxygen pressure in the laser chamber. This suggests that Nb packets oxidize at temperatures required to fully extract helium from iron-oxides in an O_2-rich environment, and are therefore not suitable for use with the high $p(O_2)$ method.

Technical implementation of the O_2 degassing procedure as an automated system is described in Supplementary Material A, along with a discussion of technical challenges, proposed solution, and long-term performance of the degassing setup. We show that the presence of O_2 during degassing does not interfere with cryogenic capture, ionization efficiency, or mass spectrometric measurement of He.

4.3. Replicate analyses

Due to the natural variability of U, Th, and Sm concentrations of samples weighing tens to hundreds of micrograms observed in some samples (see Fig. 3), some aliquots have U and Th concentrations that are several times that of the bulk of the sample. This can lead to α-ejection from high-eU areas and α-implantation into low-eU areas (Farley et al., 1996). In initial tests, we observed that ages of replicate analyses of individual samples had average ages that are close to the two-aliquot age, but showed more scatter and a slight age-eU correlation with higher ages for lower eU and vice versa, even when degassed at temperatures significantly below those for which loss of U was observed. We interpret this as an indication that the age scatter was

due to natural variability of parent isotopes and associated α-redistribution rather than a result of U-loss.

To demonstrate the capabilities of the oxygen degassing technique, we reduced the inter-aliquot variability of parent and daughter isotope concentrations by producing 12 replicate aliquots of sample MS, which were aggregated from about 10 individual grains each. These aliquots were loaded into the same small Pt tubes used for individual grains and heated to 1150 °C for 20 min. The results are given in Fig. 14. The average U concentration is slightly higher than the median value of undegassed aliquots. Sm concentrations are correspondingly higher as well, leading to Sm/U ratios that exactly match that of undegassed aliquots. Since the samples were aggregated from grains of 10-20 µg each, the U concentrations in these samples might not exactly match the median value of all undegassed aliquots.

The average of n=12 ages is 579±11 Ma (Fig. 14), which matches, within uncertainty, the age of 571±18 measured by Farley and McKeon (2015) using the two-aliquot method. This set of 12 replicate analyses shows no age-eU correlation and has Sm/U ratios, which precisely match those of undegassed aliquots. We therefore conclude that no U-loss occurred in this hematite sample during laser-heating in 130 mbar of O_2 at 1150 °C, which is more than 170 °C above the U-loss temperature in vacuum.

We also obtained ages of 1732±35 Ma and 1725±39 Ma for the highly retentive sample HM2 by holding them at 1150 °C for 4 h. This is within uncertainty of the two-aliquot age of 1761±39 Ma (Miller, 2019). These results demonstrate that the O_2 degassing method can be used to obtain precise and accurate single-aliquot (U-Th)/He ages of hematite. Sample HM1 could

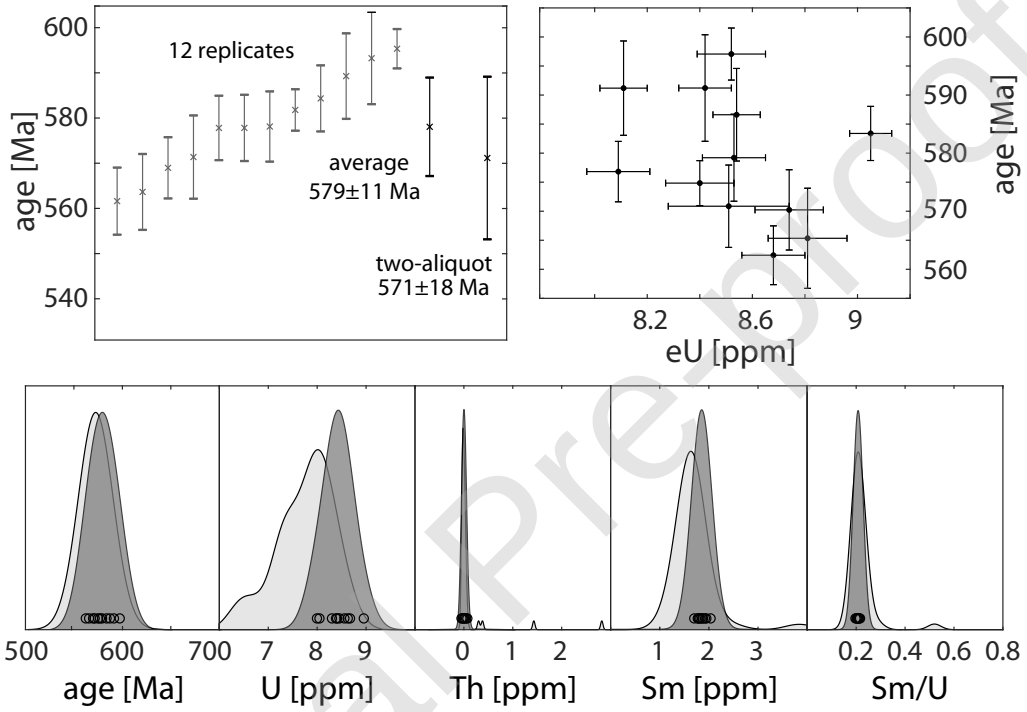

Figure 14: (U-Th)/He ages of replicate analyses of aggregated aliquots of hematite sample MS degassed in 130 mbar of O_2 at 1150 °C for 20 min, compared to the two-aliquot age of Farley and McKeon (2015). Heated aliquots show no correlation between age and effective U concentration (eU). KDE distributions of degassed samples (dark shading) overlap with those of undegassed samples (light shading). There is no indication of U-loss.

not be fully extracted even through holding at 1150 °C for 4 h and therefore this sample could not be dated. Since the sample did not show any U-loss, full helium extraction might be possible at even longer holding times. The increase in degassing temperature compared to vacuum degassing and the ability to hold samples at these temperatures for several hours without U-loss allows for the analysis of much more highly retentive hematite and goethite samples than previously possible.

4.4. Th/U and Sm/U as indicators of U-loss

The Th/U ratio is frequently used as a criterion to assess possible U-loss in iron-oxides (e.g. Danišík et al., 2013; Vasconcelos et al., 2013; Evenson et al., 2014; Ault et al., 2015; Calzolari et al., 2018; Garcia et al., 2018). However, as we show in this study, the natural variability in U and Th concentrations might obscure small amounts (<20%) of U-loss. An increase in the Th/U ratio can indicate major U-loss, provided that the normal range and distribution of U and Th concentrations have been characterized on a statistically significant number of aliquots, both degassed and undegassed. Some samples have very low Th concentrations (<0.1 ppm). Even for aliquots of hundreds of micrograms, the absolute amount of Th in these samples is close to blank level in ICP-MS analyses. The samples analyzed in this study that showed insufficient Th concentrations had Sm concentrations that were significantly higher. None of the samples studied here showed any systematic loss of Sm with temperature. We therefore utilized the Sm/U ratio, which showed the same pattern of rapid increase with U-loss as the Th/U ratio. Since Sm contributes to ^{4}He production, albeit only to a minor extent, it is routinely measured in (U-Th)/He dating of iron-oxides. In the samples

analyzed in this study, Sm concentrations and Sm/U ratios in undegassed aliquots were found to show a natural variability comparable to that of Th. The Sm/U ratio is therefore an indicator that can be used in conjunction with or in place of the Th/U ratio to detect major loss of U, if the natural variability of undegassed aliquots has been sufficiently characterized. However, the use of the Sm/U ratio is subject to the same restrictions as that of the Th/U ratio, due to the large variability in natural samples.

4.5. Age-eU correlation

Loss of U also manifests as a correlation between (U-Th)/He age and effective uranium concentration (eU = [U] + 0.235·[Th] + 0.005·[Sm]). Our data show an inverse correlation between these parameters for samples degassed in vacuum (see Fig. 15). For a sample, in which the temperatures of complete helium extraction and U-loss are close together (e.g. MS), the data closely follow the theoretical prediction of ages. If helium has been completely extracted, the increase in age is determine only by the loss of U. For the limit of no U-loss, the age-eU curve asymptotes to the true age of the sample. If the loss of U occurs at temperatures significantly below that of complete helium extraction (as in sample HM-02), the data deviate from the predicted trend (Fig. 15). Many samples have ages below the true age of the sample, and eU values close to that of undegassed aliquots, indicating incomplete He extraction and no U-loss. Aliquots, which have partially lost U with nearly complete He extraction, show ages close to the predicted trend. However, aliquots deviate from the prediction close to the true age of the sample, due to incomplete He extraction and partial U-loss. Replicate aliquots of a sample degassed in oxygen, which have no detectable U-loss,

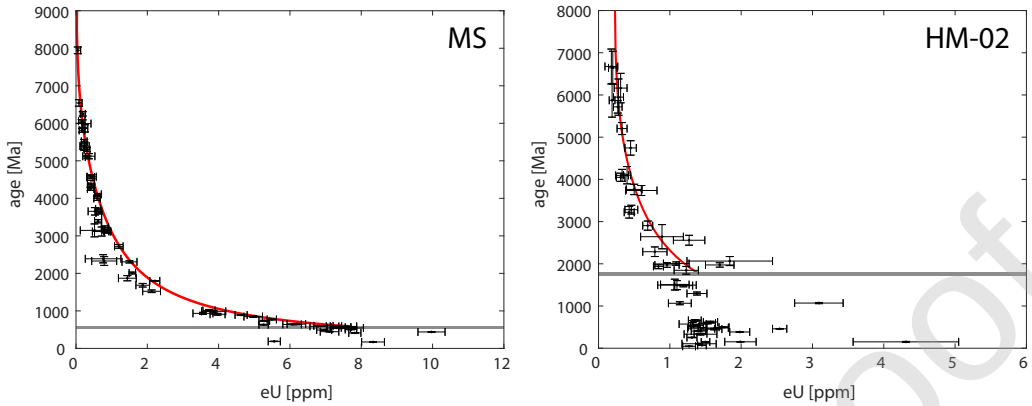

Figure 15: (U-Th)/He ages as a function of effective uranium concentration for samples MS (left) and HM-02 (right) degassed in vacuum, with bulk ages indicated by a gray line. The data shows a negative correlation between these parameters, which follows the predicted trends (red lines) assuming initial U concentrations equal to the bulk value and age variation solely due to loss of U.

show a tight clustering of ages with no age-eU correlation (Fig. 14). The shape of age-eU correlations can therefore be used as an additional tool to diagnose possible laser-heating induced U-loss.

4.6. He release in O_2

The presence of O_2 and the associated higher hematite-magnetite transition temperature relative to vacuum might affect helium extraction. The diffusion parameters of helium in magnetite are likely different than those of hematite. Preventing the phase from changing to magnetite means that helium diffusion will occur according to hematite parameters at higher temperatures than in vacuum. Additionally, the phase transition from hematite to magnetite leads to re-crystallization of the sample material, along with a change in specific density and volume as well as loss of oxygen. This might

open fractures and lead to a reduction of effective diffusion domain size or by other means promote helium loss. A resulting change in diffusivity might alter the time and temperature required to completely release helium from the sample.

5. Conclusions

We have shown that U-loss in iron-oxides correlates with the phase transition from hematite to magnetite. In vacuum, U-loss is measurable at around 980 °C in both hematite and goethite samples, although U-loss occurs at lower temperatures when samples are heated for longer periods of time. The hematite-magnetite transition temperature can be raised to ∼1250 °C with 130 mbar of oxygen partial pressure in the laser chamber during heating. The U-loss temperature is consequently raised to about 1200 °C, enabling the safe degassing of samples up to ∼1150 °C.

Samples can be held at those temperatures for several hours without detectable U-loss, which can be utilized to extract helium from highly retentive hematite samples. The phase diagram of Ketteler et al. (2001) can be used as a guide to predict the onset of the phase transition from hematite to magnetite, although we observed it up to 100 °C below the modeled temperatures. The oxygen partial pressure can then be adjusted based on the required helium extraction temperature. Time and temperature for degassing can be estimated based on the maximum domain size in the sample using the diffusion parameters of Farley (2018).

Our experiments demonstrate that temperatures during iron-oxide degassing should be tightly controlled. We have shown that temperature can be mea-

sured to within 2% accuracy using a one-wavelength pyrometer. Exceeding the temperature above which hematite readily converts to magnetite can lead to partial or total U-loss. Due to natural variability in U and Th concentrations, U-loss of 20-50% in individual samples might not be detectable as an increased Th/U or Sm/U ratio. Overheated samples responded to a hand magnet while still in the Pt packet. This test can be used to screen goethite and hematite samples which have possibly experienced loss of U as a result of partial transformation of hematite to magnetite.

We have demonstrated that it is possible to obtain reproducible single-aliquot (U-Th)/He ages of hematite samples through laser-heating to 1150°C in a pure O_2 atmosphere of about 130 mbar. The average of a set of single-aliquot ages of a hematite specimen is within uncertainty of the previously established two-aliquot age of the sample. The single-aliquot approach requires much less sample material (tens of micrograms instead of several milligrams), enabling age determination when sample material is limited. Smaller sample size also allows for the resolution of age inhomogeneity at a finer scale, which would be obscured by the homogenization necessary for the two-aliquot method.

6. Acknowledgments

We thank Hayden Miller for providing samples, sharing data, and constructive discussions. Assistance with ATR-FTIR spectroscopy from George Rossman is greatly appreciated. We thank Nathan Dalleska for his help with ICP-MS at the Environmental Analysis Center at Caltech. Peter Reiners and two anonymous reviewers are thanked for their insightful comments, which

helped to improve this manuscript.

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